

Parity effect in a small superconducting grain: A rigorous result

Guang-Shan Tian^(1,2) and Lei-Han Tang⁽¹⁾

⁽¹⁾ *Department of Physics, Hong Kong Baptist University, Kowloon Tong, Kowloon, Hong Kong*

⁽²⁾ *Department of Physics, Peking University, Beijing 100871, China*

(February 1, 2008)

The parity effect in an ultra-small superconducting grain is examined. By applying a generalized version of Lieb's spin-reflection positivity technique, we show rigorously that the parity parameter Δ_P is nonvanishing in such a system. A positive lower bound for Δ_P is derived.

74.20.Fg, 21.60.-n, 73.23.Hk, 74.80.Bj

I. INTRODUCTION

Recent experiments by Ralph, Black and Tinkham [1,2] on tunneling currents through nanometer-scale Al grains have rekindled theoretical interest in modifications of the original Bardeen-Cooper-Schrieffer (BCS) theory [3] when the average level spacing $\delta\epsilon$ becomes comparable to the bulk superconducting gap Δ . Although the possible failure of the BCS mean-field theory in this regime was speculated by Anderson [4] in 1959, quantitative studies of the crossover from ultra-small grain to bulk behavior emerged only recently [5–13].

A natural generalization of the superconducting gap Δ for a bulk superconductor to the case of a small grain with a fixed number of electrons is the parity parameter

$$\Delta_P \equiv E_0(2N+1) - \frac{1}{2}[E_0(2N) + E_0(2N+2)] \quad (1)$$

where $E_0(M)$ is the ground state energy of a grain of M electrons. Jankó, Smith, and Ambegaokar [5] first discussed the parity dependence of the superconducting gap in a small superconductor and showed that Δ_P reduces to the bulk superconducting gap Δ when the level spacing $\delta\epsilon \rightarrow 0$. Using a path integral technique, Matveev and Larkin [8] calculated Δ_P for the BCS Hamiltonian [see Eq. (2)], and found a nonvanishing result also in the ultra-small grain limit $\delta\epsilon \gg \Delta$. This is in contrast with previous mean-field calculations [6,7] which yielded a vanishing superconducting gap when the grain becomes sufficiently small. Recent numerical investigations [11,12] on specific models in the region $\delta\epsilon \approx \Delta$ have confirmed the conclusions of Matveev and Larkin, although a full analytical solution of the problem even for the simplest type of models in this class is not yet available.

The purpose of this paper is to present some rigorous results on the positivity of the parity parameter Δ_P under somewhat more general conditions than those considered so far in the literature. By applying the recently developed Lieb's spin-reflection positivity technique [14–16], we show that Δ_P is strictly positive in the BCS model of superconductivity for any value of $\delta\epsilon/\Delta$ and an arbitrary distribution of the single-particle energy levels ϵ_k (see below). In addition, we derive a lower bound for Δ_P which is independent of the number of particles in the grain.

The paper is organized as follows. In Sec. II we introduce the model and collect some of the known symmetry properties of the Hamiltonian considered. In Sec. III we introduce a generalized version of Lieb's spin-reflection positivity method and present a proof for the strict positivity of the parity parameter Δ_P . Specializing on the commonly studied case of a constant pair coupling constant, we derive a positive lower bound for Δ_P . Sec. IV contains a summary of our main results and discussions on the further possible extensions.

II. THE HAMILTONIAN AND ITS BASIC SYMMETRIES

As a plausible description of electronic states in an isolated grain of a superconductor \mathcal{M} , let us consider the BCS pairing Hamiltonian [3]

$$H_{\mathcal{M}} = \sum_{k, \sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} - \sum_{|k|, |k'| < \omega_D} g(k, k') c_{k\uparrow}^\dagger c_{k\downarrow}^\dagger c_{k'\downarrow} c_{k'\uparrow}. \quad (2)$$

Here k labels the single-particle eigenstates $|k\rangle$ of \mathcal{M} with energies ϵ_k , and $c_{k\sigma}^\dagger$ ($c_{k\sigma}$) is the fermion creation (annihilation) operator which creates (annihilates) a fermion of spin σ in state $|k\rangle$. The cut-off energy for the pairing interaction is given by $\omega_D > 0$, which, for conventional superconductors, can be taken to be the Debye frequency. The sums in (2) extend over all *admissible* states $|k\rangle$ of \mathcal{M} which satisfy the condition $|\epsilon_k| < \omega_D$. The total number of such states is denoted by N_E . The coupling constants $g(k, k')$ are assumed to be *positive* for all pairs of admissible states. In the Hamiltonian (2), only those matrix elements of the interaction responsible for superconductivity are included. The contributions of the other terms are assumed to be negligible. In particular, no pair breaking terms are present.

The average energy level spacing $\delta\epsilon = 1/\mathcal{N}(\epsilon_F)$ in a metallic grain of diameter d is proportional to $1/d$, where $\mathcal{N}(\epsilon_F)$ is the density of states at the Fermi level. In the bulk limit $d \rightarrow \infty$, the BCS mean-field theory applies and a superconducting ground state, characterized by a finite superconducting gap

$$\Delta \simeq 2\omega_D \exp(-\delta\epsilon/g), \quad (3)$$

is obtained. However, when the grain size is reduced, $\delta\epsilon$ increases and eventually becomes comparable or larger than the bulk superconducting gap Δ , at which point quantum fluctuations in the occupation numbers need to be taken into account.

The analysis presented in this paper is for a grain with a fixed number of particles. It is therefore important to note the following symmetries of the Hamiltonian (2),

(i) $H_{\mathcal{M}}$ commutes with the total fermion number operator $\hat{N} = \sum_k (\hat{n}_{k\uparrow} + \hat{n}_{k\downarrow})$, where $\hat{n}_{k\sigma} = c_{k\sigma}^\dagger c_{k\sigma}$ is the fermion number operator on state $|k\rangle$ with spin σ . Consequently, the total Hilbert space of the Hamiltonian decomposes into numerous invariant subspaces $\{V(M)\}$. Each of them is characterized by the particle number M .

(ii) Next, consider the total spin operators of the grain \mathcal{M} ,

$$\begin{aligned} \hat{S}_+ &\equiv \sum_k c_{k\uparrow}^\dagger c_{k\downarrow}, \quad \hat{S}_- \equiv \sum_k c_{k\downarrow}^\dagger c_{k\uparrow}, \\ \hat{S}_z &\equiv \frac{1}{2} \sum_k (\hat{n}_{k\uparrow} - \hat{n}_{k\downarrow}). \end{aligned} \quad (4)$$

Then, $H_{\mathcal{M}}$ also commutes with these operators. Therefore, both the total spin S and the z -component S_z are good quantum numbers. In addition, for a given M and S , states with different S_z are degenerate.

(iii) Another important property of the Hamiltonian (2) is that it does not contain pair-breaking or single-particle hopping terms. Thus, in constructing the eigenstates of the Hamiltonian, one can further restrict oneself to a subspace with a fixed proportion of paired and unpaired particles. In this subspace, the unpaired particles go into a fixed set of single-particle eigenstates, while the paired particles may choose to be in any of the remaining states. This property greatly simplifies the numerical procedure [11,12] to find the ground state of the Hamiltonian (2), although in the analysis presented in this paper we do not need to presume such behavior.

In Refs. [8], [11] and [12], the case of uniform level spacing $\epsilon_k = k\delta$ was considered. Furthermore, $g(k, k') = g > 0$ is assumed to be a constant for any pair of admissible states $|k\rangle$ and $|k'\rangle$. In the following, these conditions will be relaxed. We shall only require that $\{\epsilon_k\}$ are *real quantities* and $g(k, k') > 0$ for any pair of admissible states $|k\rangle$ and $|k'\rangle$.

III. THE PARITY PARAMETER

A. Matrix representation of wavefunction

Our result on the positivity of the parity parameter Δ_P is derived from a special representation of eigenstate wavefunctions previously used in the study of the binding energy of fermions in the negative- U Hubbard model

[17] with an odd number of particles. The idea originates from Lieb's spin-reflection positivity method [14–16] for a system with equal number of up and down spins. In the following we repeat some of the essential steps leading to the representation and refer the reader to the literature for additional details.

By regrouping the fermion operators, we can rewrite the Hamiltonian (2) as

$$\begin{aligned} H_{\mathcal{M}} &= \sum_{k, \sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} \\ &- \sum_{|\epsilon_k|, |\epsilon_{k'}| < \omega_D} g(k, k') \left(c_{k\uparrow}^\dagger c_{k'\uparrow} \right) \left(c_{k\downarrow}^\dagger c_{k'\downarrow} \right) \end{aligned} \quad (5)$$

Notice that the Hamiltonian is symmetric with respect to the up-spin and the down-spin fermion operators (spin-reflection). However, this form is not particularly convenient when we calculate matrix elements of $H_{\mathcal{M}}$ in an occupation number representation. To deal with this problem, we shall consider the so-called ‘‘pseudo-fermion’’ operators, which were first introduced by Jankó *et al.* [5] to study systematically BCS superconductivity with fixed number parity and then, re-introduced by Lieb and Nachtergaele [16] to show that the ground state of the Hubbard model at half-filling is the global ground state when the chemical potential $\mu = \frac{U}{2}$. These pseudo-fermion operators are defined by

$$\hat{C}_{k\uparrow} \equiv c_{k\uparrow}, \quad \hat{C}_{k\downarrow} \equiv (-1)^{\hat{N}_\uparrow} c_{k\downarrow} \quad (6)$$

where \hat{N}_\uparrow is the number operator of the up-spin fermions in the system. Apparently, these operators satisfy the conventional fermionic anticommutation relations

$$\begin{aligned} \{\hat{C}_{k\sigma}^\dagger, \hat{C}_{k'\sigma'}\} &= \delta_{kk'}, \\ \{\hat{C}_{k\sigma}, \hat{C}_{k'\sigma'}\} &= \{\hat{C}_{k\sigma}^\dagger, \hat{C}_{k'\sigma'}^\dagger\} = 0. \end{aligned} \quad (7)$$

However, the operators $\hat{C}_{k\uparrow}$ and $\hat{C}_{k'\downarrow}$ now *commute* with each other. Consequently, Hamiltonian (5) can be rewritten in the following direct-product form,

$$\begin{aligned} H_{\mathcal{M}} &= \sum_{k, \sigma} \epsilon_k \left(\hat{n}_{k\uparrow} \otimes \hat{I}_\downarrow + \hat{I}_\uparrow \otimes \hat{n}_{k\downarrow} \right) \\ &- \sum_{|\epsilon_k|, |\epsilon_{k'}| < \omega_D} \left(\sqrt{g(k, k')} \hat{C}_{k\uparrow}^\dagger \hat{C}_{k'\uparrow} \right) \\ &\quad \otimes \left(\sqrt{g(k, k')} \hat{C}_{k\downarrow}^\dagger \hat{C}_{k'\downarrow} \right) \end{aligned} \quad (8)$$

Using the pseudo-fermion operators, we can also write the wavefunction of a state with N_\uparrow spin-up particles and N_\downarrow spin-down particles in the form,

$$\Psi = \sum_{m=1}^{D_\uparrow} \sum_{n=1}^{D_\downarrow} W_{mn} \chi_m^\uparrow \otimes \chi_n^\downarrow. \quad (9)$$

In Eq. (9), χ_s^σ is a state vector defined by

$$\chi_s^\sigma \equiv \hat{C}_{k_1\sigma}^\dagger \cdots \hat{C}_{k_L\sigma}^\dagger |0\rangle \quad (10)$$

where (k_1, \dots, k_L) , $L = N_\uparrow$, for $\sigma = \uparrow$; $L = N_\downarrow$, for $\sigma = \downarrow$, denote the admissible states occupied by the fermions with spin σ . Apparently, the entire set $\{\chi_s^\sigma\}$ gives a natural basis for $V_\sigma(L)$, the subspace of L fermions with spin σ , whose dimension is denoted by $D_\sigma(L)$.

For the case $D_\uparrow = D_\downarrow$, it can be shown (see below) that the coefficient matrix \mathcal{W} in (9) can be brought into a diagonal form through (separate) unitary transformations in the $V_\uparrow(N_\uparrow)$ and $V_\downarrow(N_\downarrow)$ subspaces, respectively. To generalize this property to the case $D_\uparrow \neq D_\downarrow$ or equivalently $N_\uparrow \neq N_\downarrow$ (which is the case for an odd number of electrons in the grain), we consider a larger subspace $\mathcal{H}_\uparrow = V_\uparrow(N_\uparrow) \oplus V_\uparrow(N_\downarrow)$ and $\mathcal{H}_\downarrow = V_\downarrow(N_\uparrow) \oplus V_\downarrow(N_\downarrow)$, for the spin-up and spin-down particles, respectively [17]. This way the number of basis $D = D_\uparrow + D_\downarrow$ for spin-up and spin-down states becomes the same. The original wavefunction (9) can now be written in the form,

$$\Psi = \sum_{m,n} \tilde{W}_{mn} \chi_m^\uparrow \otimes \chi_n^\downarrow, \quad (11)$$

where

$$\tilde{W} = \begin{pmatrix} O & W \\ O & O \end{pmatrix} \quad (12)$$

is a $D \times D$ square matrix.

Let us now introduce the polar factorization lemma in matrix theory.

Lemma: Let A be an *arbitrary* (not necessarily Hermitian) $n \times n$ matrix. Then, there are two $n \times n$ *unitary* matrices U, V and an $n \times n$ *diagonal* semi-positive definite matrix R such that

$$A = URV, \\ r_{mm'} = r_m \delta_{mm'} \text{ and } r_m \geq 0, \quad m = 1, \dots, n. \quad (13)$$

The proof of this lemma can be found in any standard textbook of matrix theory [18] and is also presented in the appendix of Ref. [17].

Applying this lemma to $\tilde{W} = URV$, we can rewrite (11) as

$$\begin{aligned} \Psi &= \sum_{m=1}^D \sum_{n=1}^D \tilde{W}_{mn} \chi_m^\uparrow \otimes \chi_n^\downarrow \\ &= \sum_{m=1}^D \sum_{n=1}^D (URV)_{mn} \chi_m^\uparrow \otimes \chi_n^\downarrow \\ &= \sum_{l=1}^D r_l \psi_l^\uparrow \otimes \phi_l^\downarrow, \end{aligned} \quad (14)$$

where $\{r_l\}$ is a set of nonnegative numbers and

$$\psi_l^\uparrow = \sum_{m=1}^D U_{ml} \chi_m^\uparrow, \quad \phi_l^\downarrow = \sum_{n=1}^D V_{ln} \chi_n^\downarrow. \quad (15)$$

Since U and V are unitary, $\{\psi_l^\uparrow\}$ and $\{\phi_l^\downarrow\}$ are also orthonormal bases in subspaces \mathcal{H}_\uparrow and \mathcal{H}_\downarrow , respectively. Furthermore, since Ψ is an eigenvector of \hat{N}_\uparrow and \hat{N}_\downarrow , the following conditions should hold

$$\langle \Psi | \hat{N}_\uparrow | \Psi \rangle = \sum_{l=1}^D r_l^2 \langle \psi_l | \hat{N} | \psi_l \rangle = N_\uparrow, \quad (16)$$

and

$$\langle \Psi | \hat{N}_\downarrow | \Psi \rangle = \sum_{l=1}^D r_l^2 \langle \phi_l | \hat{N} | \phi_l \rangle = N_\downarrow, \quad (17)$$

where we have used the normalization condition,

$$\langle \Psi | \Psi \rangle = \sum_{l=1}^D r_l^2 = 1. \quad (18)$$

In both Eqs. (16) and (17), the spin indices are dropped in the sums, because, in each equation, only one species of spin is involved.

It is useful to note that, although the transformations U and V may mix states with different number of particles, those states ψ_l^\uparrow and ϕ_l^\downarrow which actually appear in the sum (14), i.e., those correspond to $r_l > 0$, are *eigenstates* of the number operators \hat{N}_\uparrow and \hat{N}_\downarrow , respectively. Thus,

$$\hat{N} | \psi_l \rangle = N_\uparrow | \psi_l \rangle, \quad \hat{N} | \phi_l \rangle = N_\downarrow | \phi_l \rangle, \quad \text{for } r_l > 0. \quad (19)$$

The proof is left as an exercise for the reader.

B. Parity parameter in the ground state

With these preparations, we now summarize our main result in the following theorem.

Theorem: Let $E_0(M)$ be the ground state energy of Hamiltonian (2) with M particles and Δ_P be the parity effect parameter defined in Eq. (1). Then, Δ_P is *strictly* positive for any integer N subject to $N < N_E$.

Proof: To prove this theorem, let us now consider the ground state of a system with $2N + 1$ particles and a total spin S . Since \hat{S}_+ and \hat{S}_- commute with $H_{\mathcal{M}}$, we can specialize on the case $S_z = \frac{1}{2}(N_\uparrow - N_\downarrow) = \frac{1}{2}$, i.e., $N_\uparrow = N + 1$ and $N_\downarrow = N$. Let $|\Psi_0(2N+1)\rangle$ be the ground state wavefunction with the above properties. Using the representation (14) for $|\Psi_0(2N+1)\rangle$ and the Hamiltonian (8), we can write the ground state energy of $2N + 1$ particles in the form,

$$\begin{aligned}
& E_0(2N+1) \\
& \equiv \langle \Psi_0(2N+1) | H_{\mathcal{M}} | \Psi_0(2N+1) \rangle \\
& = \sum_{l=1}^D r_l^2 \left[\langle \psi_l^\uparrow | \hat{T}_\uparrow | \psi_l^\uparrow \rangle + \langle \phi_l^\downarrow | \hat{T}_\downarrow | \phi_l^\downarrow \rangle \right] \\
& - \sum_{k,k',l_1,l_2} r_{l_1} r_{l_2} \langle \psi_{l_2}^\uparrow | \hat{Q}_\uparrow(k,k') | \psi_{l_1}^\uparrow \rangle \langle \phi_{l_2}^\downarrow | \hat{Q}_\downarrow(k,k') | \phi_{l_1}^\downarrow \rangle,
\end{aligned} \tag{20}$$

where

$$\hat{T}_\sigma = \sum_k \epsilon_k \hat{n}_{k\sigma}, \quad \hat{Q}_\sigma(k, k') = \sqrt{g(k, k')} \hat{C}_{k\sigma}^\dagger \hat{C}_{k'\sigma} \tag{21}$$

By applying inequality $|ab| \leq \frac{1}{2}(|a|^2 + |b|^2)$ to each term in the second sum of Eq. (20) and dropping the spin indices, we obtain

$$\begin{aligned}
& E_0(2N+1) \\
& \geq \frac{1}{2} \sum_{l=1}^D r_l^2 \left[\langle \psi_l | \hat{T} | \psi_l \rangle + \langle \psi_l | \hat{T} | \psi_l \rangle \right] \\
& + \frac{1}{2} \sum_{l=1}^D r_l^2 \left[\langle \phi_l | \hat{T} | \phi_l \rangle + \langle \phi_l | \hat{T} | \phi_l \rangle \right] \\
& - \frac{1}{2} \sum_{k,k',l_1,l_2} r_{l_1} r_{l_2} \langle \psi_{l_2} | \hat{Q}(k,k') | \psi_{l_1} \rangle \overline{\langle \psi_{l_2} | \hat{Q}(k,k') | \psi_{l_1} \rangle} \\
& - \frac{1}{2} \sum_{k,k',l_1,l_2} r_{l_1} r_{l_2} \langle \phi_{l_2} | \hat{Q}(k,k') | \phi_{l_1} \rangle \overline{\langle \phi_{l_2} | \hat{Q}(k,k') | \phi_{l_1} \rangle}.
\end{aligned} \tag{22}$$

The right-hand-side of the above inequality is identified with the sum of the expectation values of $H_{\mathcal{M}}$ in the two states,

$$\Psi_1 = \sum_{l=1}^D r_l \psi_l^\uparrow \otimes \bar{\psi}_l^\downarrow, \quad \Psi_2 = \sum_{l=1}^D r_l \phi_l^\uparrow \otimes \bar{\phi}_l^\downarrow, \tag{23}$$

where $\bar{\psi}_l$ and $\bar{\phi}_l$ are the complex conjugates of ψ_l and ϕ_l , respectively. To see this, we note that \hat{T}_σ is hermitian and $\{\hat{Q}_\sigma(k, k')\}$ are *real* in the representation chosen. A straightforward substitution establishes that inequality (22) is equivalent to

$$E_0(2N+1) \geq \frac{1}{2} \langle \Psi_1 | H_{\mathcal{M}} | \Psi_1 \rangle + \frac{1}{2} \langle \Psi_2 | H_{\mathcal{M}} | \Psi_2 \rangle. \tag{24}$$

From Eqs. (19), we see that, by construction, Ψ_1 and Ψ_2 are wavefunctions in the subspaces $V(N_\uparrow = N_\downarrow = N+1)$ and $V(N_\uparrow = N_\downarrow = N)$, respectively. It is easy to verify that they are also normalized,

$$\langle \Psi_1 | \Psi_1 \rangle = \langle \Psi_2 | \Psi_2 \rangle = \sum_{l=1}^D r_l^2 = 1. \tag{25}$$

Therefore, we may regard Ψ_1 and Ψ_2 as variational wavefunctions for a system of $2N+2$ and $2N$ particles, respectively. By the variational principle, we obtain,

$$E_0(2N+1) \geq \frac{1}{2} E_0(2N+2) + \frac{1}{2} E_0(2N). \tag{26}$$

In other words, $\Delta_P \geq 0$. To finish our proof, we need to show that inequality (26) is actually *strict*.

Suppose Eq. (22) holds as an equality, we must then have,

$$\langle \psi_{l_2} | \hat{C}_k^\dagger \hat{C}_{k'} | \psi_{l_1} \rangle = \overline{\langle \phi_{l_2} | \hat{C}_k^\dagger \hat{C}_{k'} | \phi_{l_1} \rangle}, \tag{27}$$

for all terms in (20) with $r_{l_1} \neq 0$, $r_{l_2} \neq 0$ and $g(k, k') > 0$. To show that this is not possible, let us consider a subset of terms with $k = k'$ and $l_1 = l_2$. Now, $\hat{C}_k^\dagger \hat{C}_{k'} = \hat{C}_k^\dagger \hat{C}_k = \hat{n}_k$. Applying Eqs. (16) and (17) to $\Psi_0(2N+1)$, we obtain

$$\sum_k \sum_{l=1}^D r_l^2 \langle \psi_l | \hat{n}_k | \psi_l \rangle = N+1, \tag{28}$$

and

$$\sum_k \sum_{l=1}^D r_l^2 \langle \phi_l | \hat{n}_k | \phi_l \rangle = N. \tag{29}$$

(Note that the expectation value of \hat{n}_k is real in any given state.) Since there are equal number of terms in the two sums, one must have at least one pair which violate Eq. (27). Consequently, when $g(k, k') > 0$ for all pairs of admissible states with $k = k'$, inequality (26) must be strict, i.e., Δ_P is strictly larger than zero.

Our proof is accomplished. **QED.**

C. Lower bound

In the above proof, we only showed that the parity parameter Δ_P is positive and nonzero. Actually, when $g(k, k') = g > 0$ is a constant for pairs of the admissible states, we can further derive a positive lower bound for Δ_P . For this purpose, we notice that inequality (22) and the ensuing inequality (26) are derived by replacing terms of the type ab in the second sum in Eq. (20) with $(|a|^2 + |b|^2)/2$. Taking into account the fact that $E_0(2N+1)$ is real, we can express the error caused by this procedure in the form $|a - b^*|^2/2$ for each term in the sum. For simplicity, let us only estimate the error produced by handling terms with $k = k'$ and $l_1 = l_2 = l$. For such terms, $\hat{C}_k^\dagger \hat{C}_k = \hat{n}_k$. Combining Eqs. (20), (22) and (24), we obtain the following inequality,

$$\Delta_P \geq \frac{g}{2} \sum_k \sum_{l=1}^D r_l^2 |\langle \psi_l | \hat{n}_k | \psi_l \rangle - \langle \phi_l | \hat{n}_k | \phi_l \rangle|^2. \tag{30}$$

Furthermore, by using the Cauchy-Schwarz inequality $|\sum_n a_n b_n|^2 \leq (\sum_n |a_n|^2) \cdot (\sum_n |b_n|^2)$, we obtain

$$\Delta_P \geq \frac{g}{2} \frac{|\sum_k \sum_l r_l^2 (\langle \psi_l | \hat{n}_k | \psi_l \rangle - \langle \phi_l | \hat{n}_k | \phi_l \rangle)|^2}{\sum_k \sum_l r_l^2}. \quad (31)$$

From Eqs. (18), (28) and (29), we obtain finally,

$$\Delta_P \geq \frac{g}{2N_E}. \quad (32)$$

Here again N_E is the number of single-particle admissible states in the relevant energy range.

IV. DISCUSSION AND CONCLUSIONS

In this paper, by applying a generalized version of Lieb's spin-reflection positivity technique, we established the existence of a nonvanishing parity parameter Δ_P in an ultra-small superconducting grain and derived a positive lower bound for Δ_P in a special case. Our study complements previous analytical work in the weak coupling regime [8] and numerical investigations [11,12]. The bound (32) may seem to be too crude for practical purposes. However, we emphasize that it is rigorous and its validity does not require the coupling constant g to be small.

An interesting open question is how pair-breaking scattering processes influence Δ_P in the ultra-small grain limit. This question has not been addressed explicitly in previous theoretical studies [5–13] based on the BCS Hamiltonian (2), which does not contain any pair-breaking interaction. In contrast, experimental work by Ralph, Black, and Tinkham [1,2] suggests that pair-breaking due to spin-orbit interactions may be quite strong in real systems. Since our method relies only on certain global symmetries of the Hamiltonian, qualitative answers to the above question can be obtained in some cases. To be more precise, let us consider separately the following two situations.

(I) *Scattering processes that preserve spin symmetry.* In such a process, the spin of the scattered electron is not flipped. A familiar example is the scattering of electrons by a nonmagnetic impurity described by the Hamiltonian,

$$H' = \sum_{k_1 \neq k_2} \sum_{\sigma} \left(t(k_1, k_2) c_{k_1, \sigma}^\dagger c_{k_2, \sigma} + C. C. \right), \quad (33)$$

where the scattering matrix $(t(k_1, k_2))$ is Hermitian. Apparently, H' is pair-breaking but it preserves the spin of the scattered electrons. We notice that the combined Hamiltonian $H = H_{\mathcal{M}} + H'$ can be formally thought to be an “extended *negative-U* Hubbard model” defined on a lattice in the *single-particle eigenstate space*. (In the literature of the strongly-correlated fermion models, such

a lattice is called a “superlattice” [19,20]). Such a model can be treated in a similar way as in Ref. [17], where the binding energy of the negative- U Hubbard model on a *real-space* lattice was discussed. By following the proof of theorem 1 in Ref. [17] and the proof of the above inequality (32), without further ado, one easily finds that the main result of this paper is still valid. Thus, the scattering of electrons by nonmagnetic impurities does not destroy superconductivity in a small superconducting grain.

(II) *Scattering processes that do not preserve spin symmetry.* In such a process, the Cooper pair is broken and the spin of the scattered electron is also flipped by the interaction. Examples include scattering by a magnetic impurity and spin-orbit interactions. While the former process definitely suppresses superconductivity in the superconducting grain, the origin and effect of the latter interaction have not been fully understood [1,2]. Due to the spin-flipping process, the total electron spin of the system is no longer a good quantum number. Consequently, our approach based on Lieb's spin-reflection positivity is not applicable to these systems. To analyze the effects of such interactions on the superconducting grain in a mathematically rigorous way, more sophisticated techniques are needed. Further research on this issue is currently under way.

Acknowledgments: One of us (G.S.T) would like to thank the Croucher Foundation for financial support and the Physics Department, Hong Kong Baptist University for their hospitality. This work is also partially supported by the Chinese National Science Foundation under grant No. 19574002.

-
- [1] D. C. Ralph, C. T. Black and M. Tinkham, Phys. Rev. Lett. **74**, 3241 (1995).
 - [2] C. T. Black, D. C. Ralph and M. Tinkham, Phys. Rev. Lett. **76**, 688 (1996).
 - [3] J. Bardeen, L. N. Cooper and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
 - [4] P. W. Anderson, J. Phys. Chem. Solids **11**, 28 (1959).
 - [5] B. Jankó, A. Smith and V. Ambegaokar, Phys. Rev. B **50**, 1152 (1994).
 - [6] J. von Delft, A. D. Zaikin, D. S. Golubev, and W. Tichy, Phys. Rev. Lett. **77**, 3189 (1996).
 - [7] R. A. Smith and V. Ambegaokar, Phys. Rev. Lett. **77**, 4962 (1996).
 - [8] K. A. Matveev and A. I. Larkin, Phys. Rev. Lett. **78**, 3749 (1997).
 - [9] F. Braun, J. von Delft, D. C. Ralph, and M. Tinkham, Phys. Rev. Lett. **79**, 921 (1997).
 - [10] F. Braun and J. von Delft, **cond-mat/9801170**.
 - [11] A. Mastellone, G. Falci, and R. Fazio, Phys. Rev. Lett.

- 80**, 4542 (1998).
- [12] S. D. Berger and B. I. Halperin, **cond-mat/9801286**.
 - [13] R. Balian, H. Flocard and M. Vénéroni, **cond-mat/9802006**.
 - [14] E. H. Lieb, in *The Hubbard model, its physics and mathematical physics*, Nato ASI Series, edited by Baeriswyl, D. K. Campbell, J. M. P. Carmelo, F. Guinea, and E. Louis (Plenum, New York, 1995), and references therein.
 - [15] E. H. Lieb, Phys. Rev. Lett. **62**, 1201 (1989).
 - [16] E. H. Lieb and B. Nachtergaele, Phys. Rev. B **51**, 4777 (1995).
 - [17] G. S. Tian, J. Phys. A: Math. Gen. **30**, 5329 (1997).
 - [18] M. Marcus and H. A. Ming, *Survey of Matrix Theory and Matrix Inequalities*, (Allyn and Bacon, Boston, 1964).
 - [19] Y. Nagaoka, Phys. Rev. **147**, 392 (1966).
 - [20] G. S. Tian, J. Phys. A: Math. Gen. **23**, 2231 (1990).